A high-efficient batch-recirculated photoreactor packed with immobilized TiO$_2$-P25 nanoparticles onto glass beads for photocatalytic degradation of phenazopyridine as a pharmaceutical contaminant: artificial neural network modeling

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ABSTRACT
In this study, removal efficiency of phenazopyridine (PhP) as a model pharmaceutical contaminant was investigated in a batch-recirculated photoreactor packed with immobilized TiO$_2$-P25 nanoparticles on glass beads. Influence of various operational parameters such as irradiation time, initial concentration of PhP, volume of solution, volumetric flow rate, pH and power of light source was investigated. Results indicated that removal percentage increases with the rise of irradiation time, volumetric flow rate and power of light source but decreases with the rise of initial concentration of PhP and volume of solution. Highest removal percentage was obtained in the natural pH of PhP solution (pH $\approx 5.9$). Results of mineralization studies also showed a decreasing trend of total organic carbon (TOC) and producing mineralization products such as NO$_3$ and NO$_2$. Modeling of the process using artificial neural network showed that the most effective parameters in the degradation of PhP were volume of solution and power of light source. The packed bed photoreactor with TiO$_2$-P25 nanoparticles coated onto glass beads in consecutive repeats have the proper ability for PhP degradation. Therefore, this system can be a promising alternative for the removal of recalcitrant organic pollutants such as PhP from aqueous solutions.

Key words | artificial neural networks, immobilized TiO$_2$-P25 nanoparticles, packed bed photoreactor, phenazopyridine

INTRODUCTION
Pharmaceutical waste disposal procedure involves a number of traditional techniques, such as sewer and incineration. Despite the widespread utilization of these techniques, they do not help with proper removal of drugs from contaminated waters, so that waste drugs flow into water resources. Therefore, proper strategies should be adopted to prevent disposing waste drugs into the environment before suitable treatment. Pharmaceuticals are a large group of medical compounds (Klavarioti et al. 2009; Epold et al. 2012; Shokri et al. 2013; Eskandarloo et al. 2016) that are used in human and veterinary activities world wide. Despite this fact that the amount of these compounds in water is not significant, the presence of them could cause serious problems in aquatic and terrestrial organisms (Chatzitakis et al. 2008; Benitez et al. 2011).

Phenazopyridine (PhP), 3-phenyldiazenylpyridine-2,6-diamine, exerts an analgesic effect on the mucosa of the urinary tract (Epold et al. 2012) and is used to provide symptomatic relief of pain in conditions such as cystitis and urethritis. Advanced oxidation processes (AOPs) such as Fenton oxidation, heterogeneous photocatalysis, electrochemical oxidation and biodegradation are applied for degradation of pharmaceutical contaminants. Among AOPs, heterogeneous photocatalysis (Fathinia & Khataee 2016) using semiconductors like titanium dioxide (TiO$_2$) have been extensively used to remove pharmaceutical compounds such as PhP.

TiO$_2$ is a widely used catalyst (Behnajady & Modirshahla 2006) in heterogeneous photocatalysis processes, due to its low cost, non-corrosiveness and great activity. When TiO$_2$ absorbs a photon with equal or higher energy...
than its band gap (3.2 eV anatase, 3.0 eV rutile phase), electron-hole pairs are produced. The pairs of electron-hole can either recombine or participate in various reactions. The mechanism of the photocatalysis process using TiO₂ is shown in Equations (1–6).

\[
\begin{align*}
\text{TiO}_2 + h\nu & \rightarrow \text{TiO}_2(e^{-}_{\text{CB}} + h^+_{\text{VB}}) \\
e^{-}_{\text{CB}} + h^+_{\text{VB}} & \rightarrow \text{TiO}_2 + \text{heat} \\
e^{-}_{\text{CB}} + O_2 & \rightarrow O_2^2^- \\
h^+_{\text{VB}} + H_2O & \rightarrow H^+ + OH^- \\
h^+_{\text{VB}} + OH^- & \rightarrow OH^- \\
h^+_{\text{VB}} + \text{PhP} & \rightarrow \text{oxidized products}
\end{align*}
\]

Slurry and immobilized photoreactors (Behnajady et al. 2006; Behnajady et al. 2007; Simonsen et al. 2008) are two kinds of heterogeneous photoreactors. Both reactors have some advantages and disadvantages. Slurry reactor provides high surface area, but it needs a system for separation of catalyst. In the immobilized system this problem is solved, although the efficiency of reaction is lower than in the slurry system (Geissen et al. 2001; Behnajady et al. 2011).

A double-cylindrical-shell photoreactor, packed with immobilized TiO₂ onto silica gel beads (Li et al. 2014) was developed for photocatalytic degradation of Rhodamine B and Methyl Orange in aqueous solution. The results showed that the developed photocatalytic reactor has proper repetitive operation performance in the removal of Rhodamine B. The removal rate of contaminant in this system is low so that 90% decolorization of Rhodamine B occurs after 12 h irradiation time. Higher irradiation time is a serious problem for practical engineering. Therefore, a key technique in order to make the environmental application of TiO₂ photocatalysis more practical seems to be the preparation of immobilized photocatalyst coatings on proper substance without loss of photocatalytic activity.

Photocatalytic reactions are complex and the kinetics of photocatalytic degradation of organic contaminants due to the spatial distribution of the radiation and presence of various radical species is hard to study. So there is a need for an appropriate technique for processing photocatalytic reactions. Artificial neural network (ANN) technique is a very promising technique for modeling complex processes (Göb et al. 2001). ANN technique was applied to model and predict the photocatalytic activity of TiO₂ nanoparticles (Frontistis et al. 2012; Behnajady & Eskandarloo 2015). They have reported that the predicted data from the designed ANN model are in good agreement with the experimental data and the designed ANN provides a reliable method for modeling the photocatalytic activity of TiO₂ nanoparticles under different operational conditions. Behnajady et al. also studied the ANN modeling for the influence of sol-gel synthesis variables on the photocatalytic activity of TiO₂ nanoparticles in the removal of Acid Red 27 (Behnajady et al. 2015). The results of their study showed that the ANN technique is a suitable technique for modeling the photocatalytic activity of TiO₂ under different synthesis conditions and provides reliable data.

In this study, the photocatalytic removal of PhP as a pharmaceutical contaminant in a batch-recirculated photoreactor (BRP) packed with immobilized TiO₂-P25 nanoparticles on glass beads is investigated and then operational parameters are modeled using ANN technique.

### MATERIALS AND METHODS

PhP was obtained from Shahre Daru drug company (Iran). The features and chemical structure of PhP are shown in Table 1. TiO₂ was Degussa P25, comprising approximately 80% anatase and 20% rutile. TiO₂-P25 had a Brunauer–Emmett–Teller (BET) surface area of 50 ± 10 m² g⁻¹ and average particle diameter of 21 nm (Behnajady et al. 2008), containing 99.5% of TiO₂. NaOH and HCl were purchased from Merck Company (Germany).

#### Table 1 | The characteristics and chemical structure of PhP

<table>
<thead>
<tr>
<th>Name</th>
<th>Phenazopyridine</th>
</tr>
</thead>
<tbody>
<tr>
<td>IUPAC name</td>
<td>3-phenyl diazenylpyridine-2,6-diamine</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C₁₁H₁₁N₅</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>213.24 g mol⁻¹</td>
</tr>
<tr>
<td>λ&lt;sub&gt;max&lt;/sub&gt;</td>
<td>430 nm</td>
</tr>
<tr>
<td>Structure</td>
<td><img src="image" alt="Structure of Phenazopyridine" /></td>
</tr>
</tbody>
</table>
Photoreactor

All of the experiments in the present study have been carried out in a BRP system comprising of a mixed tank and a packed bed photoreactor filled with TiO$_2$-P25, which have been immobilized on glass beads with 130 mL volume and 5.48 g of the catalyst loading. This photoreactor (Figure 1) is made of stainless steel with an inner diameter of 32 mm, a thickness of 2 mm, and a height of 288 mm. In the center of the photoreactor, there is a UV-C lamp (4, 6, 13 W) with an emission wavelength of 254 nm inside a quartz sleeve with an inner diameter of 20 mm and a thickness of 1 mm. In order to inject the solution inside the reactor, a peristaltic pump (Heidolph, PD5001) with adjustable flow was used. The fluid enters the photoreactor through an entrance point inbuilt on its lower part and exits from the top of the photoreactor. The immobilization of the nanoparticles on glass beads in the photoreactor is carried out by heat attachment method (Sheidaei & Behnajady 2015). The scanning electron microscopy (SEM) image of the obtained surface is shown in Figure 1.

Procedure

First, a solution with a given concentration of PhP is transferred to a mixed tank. The peristaltic pump is put in the specified flow and is ignited. After the solution is completely recirculated in the system, the light source is turned on. Then in the intervals of 15 min, samples are taken from the solution inside the mixed tank, and using spectrophotometer its absorbance in the wavelengths of 277 and 430 nm are measured, with a UV-Vis spectrophotometer (Ultrospec 2000, Biotech Pharmacia, England). This experiment is repeated in different conditions and the percentage of the removal of PhP is examined. It should be mentioned that the decline in the absorption in the 430 nm is used for calculating the rate of the breakdown of azo bond in PhP molecules and decolorization percentage. Moreover, the decline in the absorption in the 277 nm is used for calculating the removal of aromatic rings and degradation percent. Decrease of absorbance in this wavelength indicates degradation of PhP and intermediate products. Also, total organic carbon (TOC) measurement and detection of mineralization products, such as nitrate, nitrite and ammonium, are used for further mineralization studies. The measurement of oxygen was carried out by an oximeter (Oxi 538, WTW, Germany).

RESULTS AND DISCUSSION

The effect of operational parameters

The effect of the initial concentration of PhP

From a practical viewpoint, the relation between the removal percentage and the initial concentration is important and is one of the main operational parameters. Therefore, the effect of the PhP initial concentration on the removal of the
PhP was studied in the initial concentrations of 10, 20, 30 and 40 mg L⁻¹ at different irradiation times. The results of the experiments in the Figures 2(a) and 2(b) are provided for decolorization and degradation of PhP, respectively. Results indicate that, by increasing the initial concentration of PhP (Behnajady et al. 2009), removal percentage decreases. By increasing the initial concentration of PhP, the adsorption of PhP and intermediate products increased on the active sites on the catalyst bed and the photocatalyst may be saturated. Due to saturation of the photocatalyst surface, electron-hole pairs are generated and the resulting hydroxyl radicals are reduced and, thus, photocatalytic degradation percentage is reduced. The photocatalytic oxidation kinetics of many organic compounds have often obeyed pseudo-first-order kinetics (Behnajady et al. 2006; Behnajady & Modirshahla 2006; Chatzitakis et al. 2008) as follows:

\[
\ln \frac{[PhP]_0}{[PhP]} = k_{ap} t
\]

where \(k_{ap}\) is the pseudo-first-order rate constant (min⁻¹), \(t\) is the irradiation time (min), \([PhP]\) is the concentration of PhP (mg L⁻¹), and \([PhP]_0\) is the initial concentration of PhP (mg L⁻¹). According to Equation (7), \(k_{ap}\) for the removal of PhP could be calculated from the slope of straight lines of \(\ln ([PhP]_0/[PhP])\) vs. irradiation time until 45 min with linear regression analysis. In all cases, \(R^2\) (correlation coefficient) values were more than 0.98, which confirmed pseudo-first-order kinetics for the removal of PhP in this process.

A comparison between decolorization and degradation percentage in Figure 2 indicates a rapid decolorization of the solution, which proves that nitrogen-to-nitrogen double bond (\(-N= N-\)) of the PhP as the most active site for oxidative attack. A blank experiment under UV light irradiation alone (photolysis) after 30 min of irradiation time, in the case of 10 mg L⁻¹ PhP, indicates 37.5% degradation vs. 78% for photocatalysis process. Photolysis causes electronic excitation of the PhP molecules. In this situation an electron transfers from PhP excited state to ground state molecular oxygen. Subsequent reactions are recombination of the radical ions or hydrolysis of the radical cation, or homolysis to form radicals which then react with oxygen. However, the results demonstrate that 254 nm irradiation alone cannot be used as an effective procedure for the removal of organics from water (Legrini et al. 1993). Also, removal of PhP due to adsorption onto the catalyst bed was negligible (3–4%).

**The effect of the power of light source**

For this purpose, different light sources with powers of 4, 6 and 13 W were used. The result of these experiments is
shown in Figure 3. Light source power has an important role in the efficiency of photoreactor (Terzian & Serpone 1995), so that with increasing the power of light source from 4 to 13 W, PhP degradation efficiency increases from 49 to 97% at the irradiation time of 45 min. This is due to the important role of radiation in the process of photocatalysis. The more radiation intensity, more electrons are excited and, finally, the more active species to attack the PhP molecules will be available. Previous studies indicated that, at low light intensities, the reaction rate would increase linearly with increasing light intensity (Herrmann 2012). The linear relation indicates that saturation of the photocatalyst by the incident photons was not reached and electron-hole pairs are consumed more rapidly by chemical reactions than by recombination, therefore the rate of formation of the electron-hole pairs is directly proportional to the light intensity (Behnajady et al. 2007). Results in Figure 3 reveal that the UV light intensities tested in this study lie within the linear range. According to Equation (3), dissolved oxygen molecule is the main oxidant in this process which consumes photogenerated electrons. The concentration of dissolved oxygen molecule in the solution was 6.5 mg L\(^{-1}\) and decreases slightly during the process. All experiments in this work were done under air atmosphere. Rapidly moving solution tends to contain a lot of dissolved oxygen (Spellman 2013). From the air, oxygen can diffuse across the solution’s surface from the surrounding atmosphere. Therefore, decrease in the oxygen concentration is negligible.

**The effect of the volumetric flow rate**

At this stage, PhP solution prepared with an initial concentration of 10 mg L\(^{-1}\) and 500 mL volume with natural pH was tested to assess the effect of the fluid flow rate under irradiation with 13 W light source. The results of the volumetric flow rate effect in the decolorization and degradation of PhP are provided in Figure 4. Fluid flow rate influences the residence time of the liquid in the photoreactor and also the mass transfer rate and, thus, could be effective in the removal efficiency of PhP in the photoreactor. When the flow rate increases in the system, two opposite effects occur in the system, including a reduction in the residence time of solution in the photoreactor and increasing the mass transfer rate. Results indicate that by increasing the flow rate of fluid through the photoreactor bed from 60 to 220 mL min\(^{-1}\) degradation efficiency increases from 68 to 100% during the 45 min of irradiation time. Due to an increased number of passing fluids from the photoreactor, the removal efficiency increases.

On the other hand, increasing the volumetric flow rate caused a reduction of mass transfer limitations, and only the reaction rate controls the whole rate.
The effect of fluid volume

The experiments were repeated in the different volumes of fluid and the results in Figure 5 show that with increase in the volume of solution from 500 to 2,000 mL, removal percentage decreases from 97 to 31% within 45 min of irradiation time. The decrease of removal percentage with an increase in the solution volume can be related to the higher rotatable volume of solution for a given irradiation time. More wastewater volume needs longer time for treatment. In other words, for treating higher volumes of wastewater, the photoreactors with large volumes are needed (Hao et al. 2009).

The effect of the pH

The experiments were repeated at various pH and results in Figure 6 show that the decolorization and degradation percentages in the natural and acidic pH of the solution is more than the alkaline pH. The interaction of solute with TiO₂ surface is determined by surface charge of TiO₂ and ionization state of PhP. The pH of zero point charge (pH_{zpc}) represents surface charge of TiO₂ at different initial pHs. At low pH, under conditions in which pH < pH_{zpc}, the positively charged surface sites on the adsorbent increase, while at high pH, under conditions in which pH > pH_{zpc}, the negatively charged surface sites increase. The pH_{zpc} for TiO₂-P₂₅ nanoparticles is 6.25. Interactions between electron-rich PhP molecules and TiO₂ sites will be favored at low pH (pH < pH_{zpc}) (Behnajady et al. 2008), therefore oxidative degradation of PhP molecules with h{\text{VB}}^{+} occurs better and the removal efficiency increases in the pH below pH_{zpc} of TiO₂-P₂₅ nanoparticles.
Modeling of the process using ANN

The first step in the modeling is the right identification of the input and output variables. The second step is optimization of the suggested model. The topology of any neural network is determined by the number of nodes in each layer and the type of transfer function (Sabonian & Behnajady 2015).

In the present study, feed forward back propagation neural network (Figure 7) was used for modeling of the PhP removal in the BRP. This network contains six neurons in the input layer, eight neurons in the hidden layer, and one neuron in the output layer. The input variables for the ANN includes the initial concentration of PhP, the volumetric flow rate, the power of the light source, the pH of the solution, and the concentration of the PhP. The PhP degradation percentage is selected as the output variable. From 55 data, 60% were randomly selected for training, 20% for validation and 20% for testing. As the transfer function, a sigmoidal transfer function in the hidden layer and one linear transfer function in the output layer have been selected. Based on Equation (8), the data fall within the range of 0.2–0.8. The limits of the data are summarized in Table 2.

\[
A_i = 0.2 + \frac{0.6(X_i - \min(X_i))}{\max(X_i) - \min(X_i)}
\]  

(8)

Figures 8(a) and 8(b) show the efficiency chart and regression of training, validation, and tests data, respectively. Having ensured proper training of ANN, the matrix of the weights is reported in Table 3. The weights are the inter-neuron coefficients which act similarly to the synaptic power between the neurons and dendrites in biological neurons. Therefore, each of the neurons determines how much of the input neuron will be transferred to the body of the neuron. Using the matrix of the weight of the neural networks, the importance of various input variables on the output variable can be evaluated (Garson 1991).

Using the matrixes of the known weights in Table 3 and the Garson’s algorithm (Garson 1991) concerning the share of each of the operational parameters (Equation (9)), the significance of the input variables in the degradation of PhP in the BRP is calculated as shown in Table 4. It is observed that all of the operational parameters affect the degradation percentage, but the power of the light source has the greatest effect on the degradation of PhP.

\[
I_j = \frac{\sum_{m=1}^{N_h} \left( \left| W_{jm} \right| \sum_{k=1}^{N_i} \left| W_{km} \right| \right) \times \left| W_{ho} \right| \times \left| W_{om} \right|}{\sum_{k=1}^{N_h} \left( \frac{\sum_{m=1}^{N_h} \left| W_{hm} \right|}{\sum_{k=1}^{N_i} \left| W_{km} \right|} \times \left| W_{ho} \right| \times \left| W_{om} \right| \right)}
\]

(9)
where \( I_j \) is the relative importance of the \( j \)th input variable on output variable, \( N_i \) and \( N_h \) are the number of input and hidden neurons, respectively. \( W_i \) are connection weights, the superscripts ‘\( i \)’, ‘\( h \)’ and ‘\( o \)’ refer to input, hidden and output layers, respectively, and subscripts ‘\( k \)’, ‘\( m \)’, and ‘\( n \)’ refer to input, hidden and output neurons, respectively.

Also, the rank of the input variables in the degradation of PhP in the BRP is calculated by the connection weight approach. This method calculates the product of the input-hidden and hidden-output connection weights between each input and output neuron and sums the products across all hidden neurons (Olden et al. 2004). Results of this method in Table 4 indicate that the volume of solution has the greatest effect on the degradation of PhP and the power of the light source is in the second rank. Difference between results of Garson’s algorithm and the connection weight approach is logical, because Garson’s algorithm uses absolute connection weights, whereas the connection weight approach uses raw connection weights to calculate input variables’ importance. Therefore, results obtained from the connection weight approach are reliable compared with Garson’s algorithm.

### Mineralization of PhP in the BRP

In order to mineralize studies of PhP in the BRP, TOC, UV-Vis absorption peaks and important mineralization products of PhP, i.e. \( \text{NH}_4^+ \), \( \text{NO}_3^- \) and \( \text{NO}_2^- \) were measured. Figure 9(a) shows the disappearance of absorption peaks of PhP in every 15 min of irradiation time and Figure 9(b) shows the results of TOC measurement. Results of Figures 9(a) and 9(b) indicate that this photoreactor is able to mineralize PhP to a great extent, so in the irradiation time of 150 min, TOC decreases by 90%. Figures 9(c), 9(d), and 9(e) show the produced amount of nitrate, nitrite, and ammonium ions, respectively. Results show the major part of the heteroatom of N in the structure of PhP changes into ammonium and nitrate, and the amount of the produced nitrite is little. The amount of ammonium also decreases with an increase in the irradiation time while the amount of nitrate increases. Decrease in ammonium ions is attributed to their transformation into nitrate ions (Behnajady et al. 2007).

### Reusability of the BRP

Reusability of the bed is one of the major parameters in using any immobilized catalyst system. In order to study the reusability of immobilized TiO\(_2\)-P25 in the BRP, the decolorization and degradation of PhP was examined up to 24 repetitions. It is necessary to mention that after each
test, the photoreactor was washed with distilled water. Figure 10 shows that the decolorization and degradation of PhP after 24 repetitions is invariant, and there is not considerable reduction in the activity of photoreactor. In other words, the efficiency of photoreactor stays the permanent, which can be attributed to the high activity of coated
TiO₂-P25 nanoparticles. In fact, the results from reusability tests show that the TiO₂-P25 coated on glass beads has high efficiency with high reusability in the mineralization of PhP.

CONCLUSION

The results indicate that immobilized TiO₂-P25 on the glass beads in a BRP has considerable efficiency in the removal of PhP as a model pollutant from the pharmaceutical contaminants. The operational parameters such as the initial concentration of PhP, the volumetric flow rate of the fluid, the irradiation time, the power of light source, and the volume of the solution all have considerable effects on the removal of PhP. The results of mineralization analysis such as TOC and the final products (NH₄⁺, NO₃⁻/CO₃⁻ and NO₂⁻/CO₃⁻) show that there is high level of mineralization in this process. The BRP is able to both decolorize and mineralize PhP to a great extent. The major part of the heteroatom of N changes into ammonium and nitrate. Also, the results of ANN modeling show that the data obtained from ANN well matches the experimental data.

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